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(54) **Method of manufacturing of X-ray windows**

Herstellungsverfahren für Röntgenstrahlenfenster

Méthode de fabrication de fenêtres pour rayons X

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- DATABASE INSPEC INSTITUTE OF ELECTRICAL ENGINEERS, STEVENAGE, GB Inspec No. 4858883, RAVET M F ET AL 'Realization of x-ray lithography masks based on diamond membranes' & MATERIALS ASPECTS OF X-RAY LITHOGRAPHY. SYMPOSIUM, MATERIALS ASPECTS OF X-RAY LITHOGRAPHY. SYMPOSIUM, SAN FRANCISCO, CA, USA, 12-14 APRIL 1993, 1993, PITTSBURGH, PA, USA, MATER. RES. SCO, USA, pages 103-109,

## Description

The present invention relates to X-ray windows and more specifically to such windows made out of diamond.

X-ray windows as their name implies are thin, that is to say less than 10 µm, more specifically less than 1 µm, lamina which are transparent to X-rays and form part of X-ray apparatus. Often, as for example in connection with X-ray spectrometers, they need to be able to withstand pressure differentials of an atmosphere or greater. A material which is particularly suitable for use as an X-ray window is diamond. However, in thin lamina form it is weak mechanically and needs to be supported on a substrate. Existing practice is to grow the diamond from the vapour phase upon a relatively thick silicon substrate. Unfortunately silicon is a relatively heavy absorber of X-rays so that diamond on silicon X-ray windows have low X-ray transmissions.

Specification EP 0 476 827 discloses a method of manufacturing an X-ray window consisting of a layer of diamond having a supporting structure consisting of an array of diamond ribs formed upon one surface of the diamond layer. The ribs are formed by depositing a layer of diamond upon a silicon substrate, forming a patterned metal mask upon the exposed surface of the layer of diamond, depositing further diamond on the mask and exposed regions of the diamond layer, removing the mask, and finally removing the silicon substrate.

The above process has the disadvantage that the substrate and original diamond layer have to be removed from the vacuum chamber in which the diamond deposition is done in order that the mask can be deposited on the coated substrate, and returned to the vacuum chamber for the deposition of the further diamond. Not only is this time consuming, but there is no guarantee that the further deposited diamond will be epitaxial with the original diamond layer. Thus the supporting ribs may not be truly integral with the original diamond layer which could be a source of weakness in the final X-ray window. Also, diamond is a difficult material to etch, so that the removal of the mask without effecting the diamond ribs is a difficult operation.

It is an object of the present invention to provide an improved method of manufacturing a diamond X-ray window.

According to the invention there is provided a method of manufacturing an X-ray window comprising a membrane of diamond having an array of integral supporting ribs, wherein there included is the operations of

i) depositing a layer (1) of diamond upon a substrate material,

of removing the substrate material so as to provide the membrane of diamond having an array of integral supporting ribs.

Diamond may be removed from the selected areas of the exposed surface of the layer of diamond by a chemical etching process, ion beam thinning or by ablation. In the latter case, the ablation can be carried out by means of a laser which produces radiation having wavelengths in the regions of 190 to 250 nm where diamond absorbs strongly.

Preferably the substrate is made of silicon.

It is to be understood that for the purposes of the present application, the word diamond includes the material known as diamond-like carbon which has many of the properties of diamond but does not have the regular crystalline structure of diamond.

The invention will now be described, by way of example, with reference to the accompanying drawings in which

Figure 1 shows a three-dimensional view of a portion of an X-ray window embodying the invention, and

Figure 2 is a flowsheet of a process for producing a diamond window embodying the invention.

Referring to Figure 1 of the drawings, an X-ray window embodying the invention consists of a circular membrane 1 made of diamond. The membrane 1 has a plane surface 2 and a second surface 3 in which is formed an array of hexagonal depressions 4. The lands between the depressions 4 form a series of ribs 5 between the depressions 4. The result is to provide a relatively thin membrane which is integral with an array of supporting ribs. To facilitate the mounting of the X-ray window, an annulus 6 is left around the edges of the membrane 1.

The depressions may have shapes other than hexagonal, for example, they may be square-shape.

Referring to Figure 2, a process for producing an X-ray window such as that shown in Figure 1 includes the operations of

1) forming an oxide layer on the rear surface of a silicon wafer such as those used in the production of microelectronic devices.

2) Removing selectively the oxide layer from one plane surface of the wafer to form an annulus.

3) Preparing the exposed silicon surface of the wafer to provide nucleation sites for the growth of ...

4) Cleaning the prepared surface of the silicon wafer using methods which are well-known in the semiconductor art.

5) So placing the silicon wafer in a deposition chamber that the prepared surface will be exposed to the action of a gaseous reactive medium consisting of a mixture of hydrogen and methane.

6) Evacuating the reaction chamber to a pressure of about $10^{-6}$ torr, admitting a mixture of hydrogen and methane to the chamber, the methane concentration being in the range 0.5 to 1.5% by volume flow rate, establishing a plasma in the reactive medium by means of microwave radiation, a frequency of 2.45 GHz being satisfactory, maintaining a total gas pressure in the reaction chamber in the range 20 to 50 mbar, and allowing the reaction to proceed until a layer of diamond typically 10 µm thick has been formed on the exposed surface of the silicon wafer. During the deposition process, the temperature of the wafer is kept at a constant temperature between 850 and 900°C, although temperatures between 500 and 950°C can be used.

7) The wafer is removed from the reaction chamber, and using standard photolithographical techniques, an annulus of silicon oxide-nitride is produced around the edge of the silicon wafer.

8) The wafer and diamond coating are clamped to a support and the surface of the diamond layer is exposed to laser radiation through a transfer mask having an array of holes corresponding to the array of depressions 4 to be formed in the diamond membrane. The laser radiation has a frequency such as to be absorbed by the diamond, with a consequent graphitisation/ablation of the diamond. The etching of the diamond is continued until the thickness of the layer of diamond is reduced to about 1 µm. ArF (193 µm) or KrF (248 µm) are suitable lasers for the etching process.

9) The silicon wafer is then removed from the diamond membrane by means of standard chemical etching techniques.

## Claims

1. A method of manufacturing an X-ray window comprising a membrane of diamond having an array of integral supporting ribs, wherein there is included the operations of:

b) removing material from selected regions (4) of the exposed surface (3) of the layer (1) of diamond to provide the array of integral supporting ribs (5); and

c) removing the substrate material so as to provide the membrane of diamond having an array of integral supporting ribs.

2. A method according to Claim 1 wherein there is included the operations of interposing a protective mask between the exposed surface (3) of the layer (1) of diamond and a source of laser radiation, the mask being adapted to delineate those regions (4) of the exposed surface (3) of the layer (1) of diamond from which material is to be removed and subjecting the layer (1) of diamond to the said radiation until the thickness of the layer of diamond in the selected regions is reduced to a pre-determined value.

3. A method according to Claim 2 wherein the laser radiation is produced by an argon fluoride or krypton fluoride laser.

4. A method according to any preceding claim wherein the diamond is deposited by preparing a surface of the substrate to provide nucleation sites to facilitate the growth of diamond upon the said surface of the substrate, placing the substrate in a reaction chamber, evacuating the reaction chamber, admitting a mixture of hydrogen and methane to the reaction chamber, the methane concentration in the hydrogen being in the range 0.5 to 1.5 $V/_{0}$ by flow rate, establishing a plasma in the mixture of hydrogen and methane in the reaction chamber, maintaining a total gas pressure in the reaction chamber in the range of 20 to 50 mbar, maintaining the temperature of the substrate at a constant temperature within the range 500 to 900°C and terminating the reaction when a pre-determined thickness of diamond has been deposited.

5. A method according to any preceding claim wherein the initial thickness of the layer (1) of diamond is approximately 10µm and the final thickness in the selected regions (4) of the diamond layer (1) is approximately 1µm.

## Patentansprüche

1. Verfahren zur Herstellung eines Röntgenfensters [illegible]

terial abscheidet

b) Material aus ausgewählten Bereichen (4) der freiliegenden Oberfläche (3) der Diamantschicht (1) entfernt, um die Anordnung integraler Stützrippen (5) zur Verfügung zu stellen und

c) das Substratmaterial entfernt, um die Diamantmembran mit einer Anordnung integraler Stützrippen zur Verfügung zu stellen.

2. Verfahren nach Anspruch 1, bei dem man zwischen die freiliegende Oberfläche (3) der Diamantschicht (1) und eine Laserstrahlenquelle eine Schutzmaske legt, welche so ausgelegt ist, daß sie die Bereiche (4) der freiliegenden Oberfläche (3) der Diamantschicht (1), von denen Material entfernt werden soll, abgrenzt, und die Diamantschicht (1) bestrahlt, bis die Dicke der Diamantschicht in den gewählten Bereichen auf einen vorher festgelegten Wert verringert ist.

3. Verfahren nach Anspruch 2, bei dem die Laserstrahlung durch einen Argonfluorid- oder Kryptonfluoridlaser erzeugt wird.

4. Verfahren nach einem der vorstehenden Ansprüche, bei dem der Diamant dadurch abgeschieden wird, daß man eine Oberfläche des Substrats präpariert, um das Diamantwachstum auf der Oberfläche des Substrats erleichternde Keimbildungsstellen zur Verfügung zu stellen, die Reaktionskammer evakuiert, eine Mischung aus Wasserstoff und Methan in die Reaktionskammer einleitet, wobei die Methankonzentration im Wasserstoff im Bereich von 0,5 bis 1,5 Vol-% auf Basis der Fließgeschwindigkeit liegt, das Gemisch aus Wasserstoff und Methan in der Reaktionskammer in ein Plasma überführt, den Gasgesamtdruck in der Reaktionskammer im Bereich von 20 bis 50 mbar und die Temperatur des Substrats im Bereich von 500 bis 900°C konstant hält, und die Reaktion dann beendet, wenn der Diamant bis zu einer vorher festgelegten Dicke abgeschieden wurde.

5. Verfahren nach einem der vorstehenden Ansprüche, bei dem die anfängliche Dicke der Diamantschicht (1) annäherungsweise 10 µm und die Enddicke in den ausgewählten Bereichen (4) der Diamantschicht annäherungsweise 1 µm beträgt.

## Revendications

suivantes

a) le dépôt d'une couche (1) de diamant sur un matériau de substrat

b) l'extraction du matériau de régions choisies (4) de la surface exposée (3) de la couche (1) de diamant pour la formation de l'arrangement des nervures de support (5) qui en sont solidaires, et

c) l'extraction du matériau du substrat afin qu'une membrane de diamant ayant un arrangement de nervures de support qui en sont solidaires soit réalisée.

2. Procédé selon la revendication 1, qui comprend des opérations d'interposition d'un masque protecteur entre la surface exposée (3) de la couche (1) de diamant et une source d'un rayonnement laser, le masque étant destiné à délimiter les régions (4) de la surface exposée (3) de la couche (1) de diamant dont le matériau doit être extrait, et l'exposition de la couche (1) de diamant audit rayonnement jusqu'à ce que l'épaisseur de la couche de diamant dans les régions choisies soit réduite à une valeur prédéterminée.

3. Procédé selon la revendication 2, dans lequel le rayonnement laser est produit par un laser à fluorure d'argon ou à fluorure de krypton.

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel le diamant est déposé par préparation d'une surface du substrat afin qu'elle forme des sites de nucléation qui facilitent la croissance du diamant sur ladite surface du substrat, par disposition du substrat dans une chambre de réaction, par évacuation de la chambre de réaction, par admission d'un mélange d'hydrogène et de méthane dans la chambre de réaction, la concentration du méthane dans l'oxygène étant comprise entre 0,5 et 1,5 % en volume en débit, par établissement d'un plasma dans le mélange d'hydrogène et de méthane dans la chambre de réaction, par maintien d'une pression totale du gaz dans la chambre de réaction entre 20 et 50 mbar, par maintien de la température du substrat à une température constante comprise dans la plage allant de 500 à 900 °C, et par interruption de la réaction lorsqu'une épaisseur prédéterminée de diamant s'est déposée.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'épaisseur initiale de la couche (1) de diamant est d'environ 10 µm et

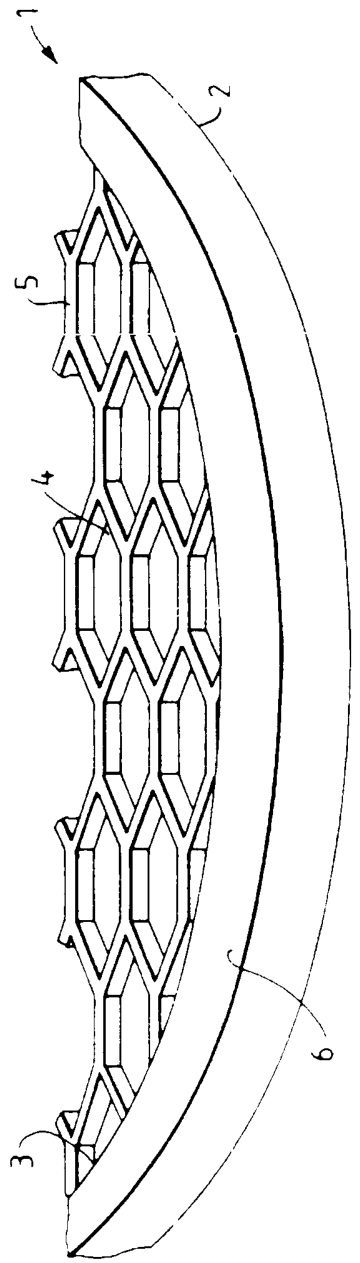


Fig. 1

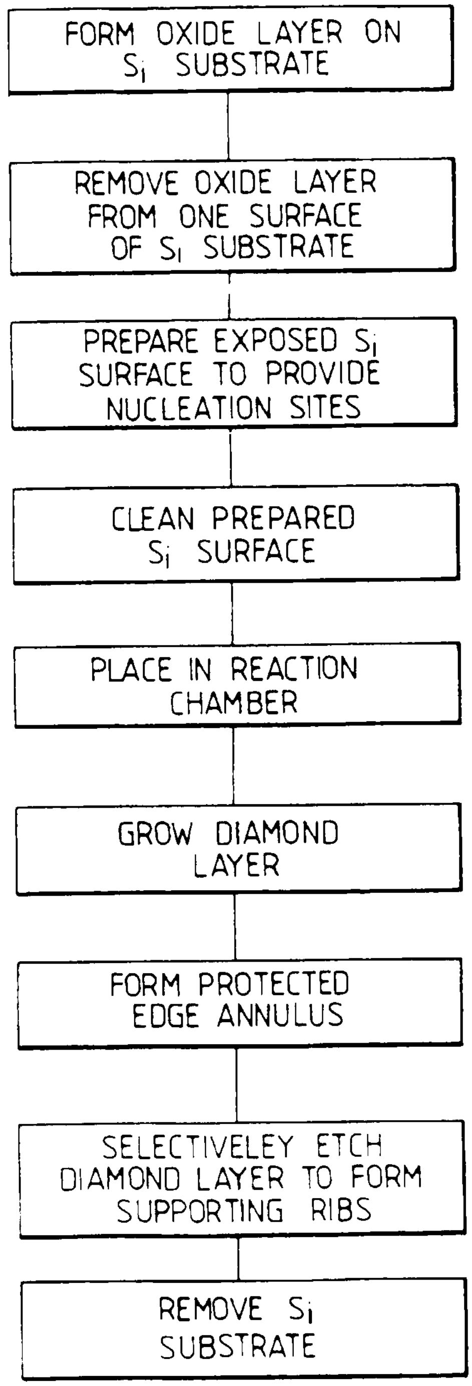
FORM OXIDE LAYER ON Si SUBSTRATE
REMOVE OXIDE LAYER FROM ONE SURFACE OF Si SUBSTRATE
PREPARE EXPOSED Si SURFACE TO PROVIDE NUCLEATION SITES
CLEAN PREPARED Si SURFACE
PLACE IN REACTION CHAMBER
GROW DIAMOND LAYER
FORM PROTECTED EDGE ANNULUS
SELECTIVELEY ETCH DIAMOND LAYER TO FORM SUPPORTING RIBS
REMOVE Si SUBSTRATE

Fig. 2